Renewable and Sustainable Energy Reviews 18 (2013) 184–193

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Overview of the production of biodiesel from Waste cooking oil

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ARTICLE INFO

Article history:
Received 4 July 2012
Received in revised form
10 October 2012
Accepted 10 October 2012
Available online 10 November 2012

Keywords:
Waste cooking oil
Vegetable oil
Biodiesel
Methyl ester
Transesterification
Renewable energy

ABSTRACT

In recent years, biodiesel has attracted significant attention from researchers, governments, and industries as a renewable, biodegradable, and non-toxic fuel. However, several feedstocks have been proven impractical or infeasible because of their extremely high cost due to their usage primarily as food resources. Waste cooking oil (WCO) is considered the most promising biodiesel feedstock despite its drawbacks, such as its high free fatty acid (FFA) and water contents. This review paper provides a comprehensive overview of the pre-treatment and the usage of WCO for the production of biodiesel using several methods, different types of reactors, and various types and amounts of alcohol and catalysts. The most common process in the production of biodiesel is transesterification, and using a methanol–ethanol mixture will combine the advantages of both alcohols in biodiesel production. In addition, this paper highlights the purification and analysis of the produced biodiesel, operating parameters that highly affect the biodiesel yield, and several economic studies. This review suggests that WCO is a promising feedstock in biodiesel production.

Contents

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http://dx.doi.org/10.1016/j.rser.2012.10.016

1. Introduction

Biodiesel from renewable resources is one of the most attractive alternative fuels currently being developed because of its low emissions and its desirable chemical characteristics, such as being non-toxic, biodegradable [1], and carbon neutral [2]. Additionally, biodiesel fuel can be used in any conventional diesel engine, unlike non-renewable fuel (petroleum or diesel). Non-renewable fuel also lasts for a limited time and emits pollutants, such as nitrogen, sulphur, and carbon oxides, lead, hydrocarbons, etc. [3].

Cooking oil sources differ across the globe. Their base materials are plant-based lipids, such as corn oil, margarine, coconut oil, palm oil, olive oil, soybean oil, grape seed oil and canola oil, or animal-based lipids, such as butter, ghee, kermanshahi oil and fish oil. In Malaysia, the most common cooking oil is made from oil palm because of its low cost relative to other sources, such as coconut, corn or soybean plants. Biodiesel is produced by the transesterification of these lipids. Previous studies have shown that biodiesel can be produced from various types of vegetable oil, such as sunflower oil, palm oil and soybean oil [4–6].

However, the use of a food source (edible oil) to produce biodiesel at the expense of the millions of people facing hunger and starvation around the world has received harsh criticism from several non-governmental organisations (NGOs) worldwide [2] due to the resultant increase in the demand for vegetable or edible oil and unnecessary clearing of forests for plantation. Deforestation will disturb animal and plant ecosystems. The use of WCO as a biodiesel feedstock could reduce such problems as water pollution and blockages in water drainage systems, which require extra work to clean. However, there is also a growing concern regarding the environmental impact of an increase in the production of WCO in homes and restaurants [7].

WCO can be freely collected from restaurants and houses using a special “recycle bin” placed in each restaurant or house, which may require public awareness campaigns preceding the collection process. In Malaysia, NGO volunteers conducted an awareness campaign on the environmental impact caused by the direct discharge of WCO into the drainage system. These volunteers inform the community that disposing of WCO via drainage or a landfill could cause water and soil pollution and disturb the aquatic ecosystem in addition to being a human health concern. They also alerted the community to the negative effects of using recycled WCO as cooking media in food preparation. The NGO will establish a collection centre and arrange for the community to appoint a representative to collect the WCO. The WCO will be collected monthly, and payment will be made to the community fund. Finally, the collected WCO will be sent to the diesel manufacturer and factory.

Although state-of-the-art biodiesel production from WCO is less profitable than the use of fossil fuels, research is still on-going to improve the yield and quality of the fuel. Again, because the more fossil fuels are used each year than are produced, WCO is an excellent alternative. Additionally, this practice could prevent the recycling of WCO for cooking, which is being performed by some companies. Cooking oil recycled from WCO is believed to cause cancer because of the toxic contents produced when the oil is oxidised. However, obtaining WCO in large amounts remains a concern. Future studies should compare the methods used by other countries: their pros and cons, implementation, and economic impact. In London, Uptown Oil supplies fresh cooking oil to selected Western restaurants and pubs with a current average return of approximately 60% of the fresh oil. Their supplier has been trained to maximise the quality of the obtained WCO to reduce the impurities and ease the transformation process to biodiesel. The company collects and processes the WCO and produces recycled biodiesel directly in their plant. The biodiesel is then sold on the premises, especially to London black taxis. A strong relationship with local authorities offers direct contact with public facilities and institutions, such as hospitals, airports, schools, and catering services. Uptown also provides an eco-friendly window sticker to restaurants that supply the WCO in recognition of their co-operation [8].

2. Biodiesel

“Biodiesel” has been defined by the American Society for Testing and Materials (ASTM) as a monoalkyl ester of fatty acids or fatty acid (m)ethyl ester [3] derived from renewable feedstocks, such as vegetable oils. The term “bio” indicates the biological source of biodiesel, in contrast with conventional diesel [9]. Biodiesel is a clear liquid with a light- to dark-yellow colour. It has a boiling point of over 200 °C, a flash point between 145–175 °C, a distillation range of 195–325 °C, and a vapour pressure (mm Hg at 22 °C) less than 5. It is also insoluble in water, has a light musty/soapy odour, is biodegradable, and has stable reactivity. However, strong oxidising agents must be avoided [3].

Direct use and blending, micro-emulsification, pyrolysis, and transesterification have been used in the production of biodiesel from vegetable oil [3,10]. The most common process in the production of biodiesel is transesterification, which involves alcohol and vegetable oil in the presence of a catalyst to yield biodiesel and glycerol [11]. Using this method, the biodiesel produced has a lower viscosity, preventing serious engine damage because of incomplete combustion and poor fuel atomisation. The most commonly used alcohol in this process is methanol because of its low cost. The use of methanol produces methyl esters with several outstanding advantages over other new renewable fuels, such as being a clean engine fuel, a lower molecular weight by one-third, a lower viscosity by approximately one-seventh, a slightly lower flash point, marginally increased volatility, and considerably reduced pour point. The most significant variables affecting biodiesel yield during transesterification are the reaction temperature and the molar ratio of alcohol to vegetable oil [3].

Several edible and non-edible oils, such as sunflower oil, palm oil, soybean oil, rapeseed oil, jatropha seed oil, neem oil, rubber seed oil, microalgae oil, silk cotton tree oil, and WCO, have been used as biodiesel feedstocks [3,6]. Biodiesel is superior to petroleum-based diesel because it is renewable, biodegradable, non-toxic, relatively environmentally friendly [12], has low emissions and sulphur content, high lubricity, aromatic content, and better flash point and ignition properties [10,13]. Table 1 compares the properties of biodiesel from WCO and commercial diesel fuel [14]. Biodiesel faces few technical problems in terms of storage stability, low-temperature properties, NO_x exhaust

Table 1
Comparison of properties between biodiesel from WCO and commercial diesel fuel.

Fuel property	Units	Biodiesel from WCO	Commercial diesel fuel
Kinematic viscosity (40 °C)	mm^2/s	5.3	1.9–4.1
Density	kg/L	0.897	0.075–0.840
Flash point	K	469	340–358
Pour point	K	262	254–260
Cetane number		54	40–46
Ash content	%	0.004	0.008–0.010
Sulfur content	%	0.06	0.35–0.55
Carbon residue	%	0.33	0.35–0.40
Water content	%	0.04	0.02–0.05
Higher heating value	MJ/kg	42.65	45.62–46.48
FFA	mgKOH/g	0.10	–

emissions [15], high cost of feedstock, and its feedstock being a food resource priority [2]. It is currently attracting global attention as a blending component or direct replacement for diesel fuel in vehicle engines. Typically, biodiesel fuel contains less alkyl fatty acids (chain length C14–C22) and esters of short-chain alcohols, mainly, methanol or ethanol. As it has very similar characteristics to fossil diesel fuel, it can be used in any mixture of petrodiesel fuel. However, it has lower exhaust emissions [3]. Biodiesel has high HHVs (higher heating values) (42.65 MJ/kg), which are higher than those of coal (32–37 MJ/kg) [14,16] and comparable to those of other commercial fossil fuels, such as gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg). Biodiesel methyl ester improves the lubricity of a diesel fuel blend, reduces long-term engine wear in diesel engines and is a 66% better lubricant than petrodiesel [17]. Compared with petrodiesel, biodiesel faces few operating disadvantages, such as cold start problems, poor low-temperature flow properties, lower energy content, high copper strip corrosion, and fuel pumping difficulty from higher viscosity and measured in terms of cloud point, pour point, and cold filter plugging point (CFPP). The low-temperature properties are not applicable to aviation applications [10]. Biodiesel is currently more expensive to produce than petrodiesel, which appears to be the primary factor preventing its more widespread use. Current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use [4]. Biodiesel is a technologically feasible alternative to fossil diesel, but biodiesel costs 1.5–3 times more than fossil diesel. Regarding actual fuel costs, the current cost of biodiesel is comparable with that of gasoline [3,10].

3. Properties of WCO and its feedstock potential

WCO is obtained after using edible vegetable oils [5], such as palm, sunflower, and corn oils, several times for frying. The chemical and physical properties of WCO are slightly different from those of fresh oils because of the changes that occur during frying [18]. Table 2 shows the chemical and physical properties of a WCO sample collected by Wen et al. [19].

The amounts of WCO generated by homes and restaurants are increasing rapidly due to the tremendous growth in human population [7]. Moreover, the increment in food consumption has also contributed to the production of huge amounts of WCO [13]. Table 3 shows the estimated amounts of WCO generated in selected countries and the oil source. The United States alone generates approximately 10 million tons of WCO annually [20], which requires an economical and environmentally friendly disposal method, such as utilisation as feedstock for biodiesel production [2,7].

On the other hand, the cost of WCO is 2 and 3 times less than that of fresh vegetable oil, which leads to a significant reduction in the total processing cost [13]. Moreover, the use of WCO is not at the expense of food resources, such as in the use of virgin edible oils, which eliminates any possible controversy in this matter [2]. One of the drawbacks in using WCO for the production of biodiesel is that it contains several impurities, such as free fatty acid (FFA) and water, that must be treated before transesterification because of their significant adverse effects on the process [26]. The quality of WCO is estimated with regard to its acid and saponification values. Transesterification failure may occur if the FFA content in the oil is above 3% [27].

Table 2
Physical and chemical properties of WCO.

Property	Units	Value
Palmitic acid	wt%	8.5
Stearic acid	wt%	3.1
Oleic acid	wt%	21.2
Linoleic acid	wt%	55.2
Linolenic acid	wt%	5.9
Others	wt%	4.2
Water content	wt%	1.9
Density	cm^3/g	0.91
Kinematic viscosity (40 °C)	mm^2/s	4.2
Saponification value	mgKOH/g	207
Acid value	mgKOH/g	3.6
Iodine number	$gI_2 100\ g^{-1}$	83
Sodium content	mg/kg	6.9
Peroxide value	mg/kg	23.1

Table 3
Quantity of WCO generated in various countries around the world.

Country	Quantity (million tones/year)	Source of oil	Ref.
United States	10	Soybean oil	[20]
China	4.5	Salad oil, animal fat	[20]
European	0.7–10	Rapeseed oil, sunflower oil	[21]
Japan	0.45–0.57	Soybean oil, palm oil, animal fat	[22]
Taiwan	0.07	Soybean oil, palm oil, beef oil, lard oil	[23]
Malaysia	0.5	Palm oil	[20]
Canada	0.12	Animal fat, canola oil	[20]
England	1.6	Soybean oil, canola oil	[24]
Ireland	0.153	Rapeseed oil	[25]

4. Pretreatment of WCO

One of the main drawbacks of using WCO as feedstock in biodiesel production is the presence of unwanted contents, such as FFA, water [2], and other solid impurities [28]. The presence of water in the oil sample often leads to hydrolysis, and a high FFA content leads to saponification. Both reactions result in low biodiesel yield [1] and catalyst consumption [2]. To reduce the high FFA content in the oil, several techniques have been proposed, such as acid esterification with methanol and sulphuric acid [28], esterification with ion-exchange resins [29], neutralisation with alkalis followed by soap separation by a decanter, and extraction with polar liquids along with acid esterification and distillation of FFA [18]. To eliminate water content, a WCO sample is often heated to above 100 °C [14,27]. Alternatively, vacuum distillation (0.05 bar) is used at the industrial scale [30]. Furthermore, suspended solids, phospholipids, and other impurities can be washed away with hot water [28] or removed by centrifugation [14] and paper filtration [7].

5. Transesterification

The most practical and common way of producing biodiesel is by transesterification (also called methanolysis) [31], which is a catalysed reaction of vegetable oil in the presence of alcohol to yield biodiesel and glycerol [32,33]. In transesterification, glycerol in triglycerides is replaced with a short-chain alcohol [34]. The process starts with a sequence of three consecutive reversible reactions, wherein triglycerides are converted to diglycerides, diglycerides are converted to monoglycerides, and monoglycerides are converted to glycerol. Each step produces an ester and, as a consequence, generates three ester molecules from one triglyceride molecule [35]. The transesterification chemical equation is shown in Fig. 1.

Previous reports and research have shown that biodiesel production by transesterification can be catalysed using homogeneous

catalysts (acid and alkali) and heterogeneous catalysts (acid, alkali, and enzyme) [4]. Nevertheless, acid and alkali transesterification processes have been proven to consume less time and have a lower cost than enzyme-catalysed processes. A catalyst splits oil molecules, and an alcohol (ethanol or methanol) combines with a separate ester to produce alkyl ester (ethyl or methyl) [3]. However, the use of alkali catalysts is quite difficult when the FFA content is high, despite its high biodiesel yield and the high purity of the products [36]. The challenge of high FFA content could be overcome by esterification using sulphuric acid and methanol [3]. Fig. 1 shows the transesterification reaction of triglycerides with alcohol. A catalyst is usually used to improve the reaction rate and yield. Considering that the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. This transesterification involves a simple process that produces biodiesel with physical characteristics almost identical to those of fossil diesel fuel, lowers the viscosity, and gives glycerol as a byproduct, which is marketable and valuable [3]. In the following section, several techniques in biodiesel production, using various types of catalysts, are highlighted in detail.

5.1. Homogeneous-catalysed transesterification

Homogeneous catalysts can be base catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) [37], or acid catalysts, such as sulphuric, sulphonic, phosphoric, and hydrochloric acids [38]. Base catalysts are preferred over acid catalysts because they have higher catalytic efficiency, lower cost [19], and lower reaction temperature and pressure [31]. However, base catalysts may react with FFA present in the feedstock during transesterification, resulting in soap formation by saponification, which may consume the catalyst and reduce its efficiency [14].

Several studies have been carried out to identify the best homogeneous catalyst for biodiesel production from WCO. Shimada et al. [37] stated that potassium hydroxide was considered the best catalyst for transesterification using WCO. Demirbas [14] proposed the use of an additional amount of potassium hydroxide to overcome the saponification problem, whereas Vicente et al. [39] suggested the use of basic methoxide catalysts, such as sodium and potassium methoxides, because their structures lack the (OH) group necessary for saponification. On the other hand, Soriano et al. [40] affirmed that acid catalysts might be more suitable for waste oils (with high FFA content), although the reaction is slower and requires a greater amount of excess alcohol. Nevertheless, two-step catalysed transesterification has been proven effective in the production of biodiesel from feedstock that contains a large amount of FFA [41,31,42–47]. In this method, both acidic and basic catalysts are used separately: the acidic catalyst, such as ferric sulphate [42] or sulphuric acid, is used in the first step, the esterification of FFA, whereas the basic catalyst is used in the second step, in the triglyceride's transesterification [44]. However, in this method, catalysts are removed after each step, according to Bautista et al. [44]. In contrast, Guzatto et al. [41] used a modified double-step process, which uses the basic catalyst in the first step and the acidic catalyst in the second, reducing the overall process time and catalyst concentration. In addition, Çaylı and Küsefoğlu [43] used basic catalysts in both steps of their method, claiming that this method can be easily modified to become a continuous process.

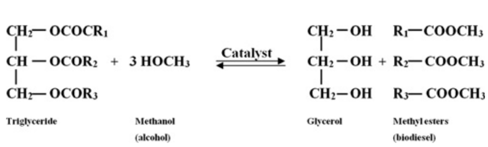


Fig. 1. Transesterification chemical equation [28].

5.2. Heterogeneous-catalysed transesterification

Heterogeneous catalysts have caught researchers' attention recently because of their advantages over homogenous catalysts in terms of higher biodiesel yield; higher glycerol purity [48]; easier catalyst separation and recovery [11,19]; being cheaper, safer, and more environmentally friendly; and not requiring a washing step for the crude ester [49]. Moreover, heterogeneous catalysts are preferred over homogenous catalysts in biodiesel production from WCO because saponification and hydrolysis reactions are eliminated [1].

Just like homogeneous catalysts, heterogeneous catalysts are also of two types, namely, acidic and basic. Examples of heterogeneous acid catalysts are sulphated metal oxide, heteropolyacids, acidic ion exchange resin, and sulphonated amorphous catalysts [50]. Chakraborty and Sujit generated a novel Ni–Ca-hydroxypatite solid acid catalyst using pretreated waste fish scale as a support through the wet impregnation of $Ni(NO_3)_2 \cdot 6H_2O$ (59.9% yield of biodiesel) [51]. Additional examples of heterogeneous base catalysts include zinc oxide (ZnO), calcium oxide (CaO), strontium oxide (SrO) [11], and Na/SiO_2 [52,53]. Empty fruit bunch (EFB) ash doped with KOH is another type of organic heterogeneous base catalyst. Using EFB, the biodiesel obtained is 98% higher in specifications than those in European biodiesel quality standard EN 14214 [54]. Recently, Chakraborty et al. used calcined washed Rohu fish scale (*Labeo rohita*) as a heterogeneous base catalyst with a maximum biodiesel yield of 97.73% and up to six reuses [55]. Fly-ash-supported CaO catalyst from eggshell waste has also been generated, with a performance of 96.5% for biodiesel [56]. Basic heterogeneous catalysts have higher activity than acidic catalysts, which require longer reaction times and higher temperatures [50]. Akbar et al. [52] used a solid catalyst, Na/SiO2, and the sol–gel method to obtain an optimum conversion of 99% for a relatively short reaction time of 45 min under a mild conditions (65 °C, with a 1:15 M ratio of methanol to oil and a catalyst amount of 6 wt%). Hence, the development of heterogeneous catalysts that can reduce the costs and the problems associated with homogeneous catalysts is crucial [52,53]. Table 4 reviews selected heterogeneous catalysts used in the production of biodiesel from WCO and other virgin oils [57].

Table 4
Review of biodiesel production using heterogeneous catalysts.

Oil	Catalyst	Catalyst amount (wt%)	Alcohol molar ratio	Process Temperature & time (°C, h)	Ester yield (%)
WCO	Sr/ZrO2	2.7	29:1	115.5, 2.82	79.7
WCO	ZS/Si	3.0	6:1	200, 10	81.0
Waste oil	SO_4^{2-}/TiO2–SiO2	3.0	9:1	200, 5	92.0
Palm oil	CaO/Al2O3	3.5	12:1	65, 5	94.0
Soybean	Na2MoO4	5.0	54:1	65, 3.5	96.8
Triolein	HPNbW/W-Nb	11.0	15:1	100, 8	81.0

However, heterogeneous catalysts may not be practical at an industrial scale because of their high excess alcohol requirements, high reaction temperatures, long reaction times, and high energy consumption [11].

5.3. Enzyme-catalysed transesterification

Biocatalysts (enzymes) have been investigated as the means to overcome the challenges presented by chemical catalysts. Lipase, the most commonly used enzyme in biodiesel production, is an effective catalyst that converts all of the FFA content in the WCO to fatty acid methyl ester [58]. Moreover, when lipase is used to catalyse transesterification reaction, glycerol can be recovered easily, biodiesel can be purified in a simple way, the water content of oil can be tolerated to avoid saponification, the process results in a higher biodiesel yield [4], and the reaction can be carried out at lower temperature and pressure, which reduces energy consumption [59]. However, enzyme-catalysed transesterification is not yet used at an industrial scale for several reasons, such as the high cost of lipase, inhibition of lipase by methanol [60], glycerol adsorption on lipase, and long reaction time [61]. Table 5 compares biocatalysts and chemical catalysts (basic and acidic) for use in biodiesel production [62].

Lipase is extracted from several sources, such as microbial sources (fungi and bacteria), animals, and plants. However, lipase from microbial sources is the most commonly used because of its low production cost and simple modification [63]. Using lipase in an immobilised form is important because it facilitates its reuse in several batches [58]. Several studies have used lipases immobilised onto several supports, such as macroporous supports (adsorption), hydrophobic sol–gel support (entrapment), silica aerogel (encapsulation), and chitin (chemical binding) [4].

Several lipases have been implemented in biodiesel production from WCO, such as *Candida Antarctica* (Novozyme 435) [7,64–66], *Thermomyces lanuginose* [4,66], *Mucor miehei* [58,67], *Geotrichum* sp [47], *Penicillium expansum* [68], *Aspergillus oryzae* [64], *Rhizopus oryzae* [69], *Bacillus subtilis* [70], *Candida rugosa*, *Pseudomonas cepacia*, and *Pseudomonas fluorescens* [66]. However, several studies have proven that *C. Antarctica* (Novozyme 435) is the most efficient lipase in biodiesel production because it contributes to a high conversion percentage and can be reused for over 50 reaction batches [61,71]. Nevertheless, *Thermomyces lanuginosus* can be an alternative to *C. Antarctica* (Novozyme 435), sometimes providing higher reaction rates by increasing the load of alcohol [72]. Table 6 reviews several lipases used in WCO esterification.

5.4. Non-catalysed transesterification

As a result of the drawbacks of most of the catalysts (chemicals and enzymes) mentioned in the previous sections, a non-catalytic method with supercritical methanol has been developed [73,74]. A supercritical transesterification process has several advantages over the conventional process in terms of the elimination of catalysts, easier separation of products, faster reaction rate, elimination of FFA and water contents on the ester yield [5],

Table 7
Comparison of properties between conventional and supercritical transesterification.

Property	Supercritical	Conventional
Catalyst need	No (+)	Yes
Reaction time	S–min	Min–h
Temperature (°C)	200–300	50–80
Pressure (bar)	100–200	1
FFA sensitive	No (+)	Yes
Water sensitive	No (+)	Yes
Pre-treatment	No (+)	Yes
Catalyst removal	No (+)	Yes
Soap removal	No (+)	Yes

Table 5
Comparison between biocatalysts and chemical catalysts for use in biodiesel production.

Parameter	Enzymatic process	Chemical process	
		Alkaline process	Acid process
FFA content in the raw material	FFA are converted to biodiesel	Soaps formation	FFA are converted to biodiesel
Water content in the raw material	It is not deleterious for lipase	Soaps formation. Oil hydrolysis resulting more soaps	Catalyst deactivation
Biodiesel yield	High, usually around 90%	High, usually $>96\%$	High yields ($>90\%$) only for high alcohol to oil molar ratio, high catalyst concentration and high temperature
Reaction rate	Low	High	Slower than for alkaline process
Glycerol recovery	Easy, high grade glycerol	Complex, low grade glycerol	Complex, low grade glycerol
Catalyst recovery and reuse	Easy reusability proved but not sufficiently studied.	Difficult; neutralized by an acid Partially lost in post-processing steps	Difficult, the catalyst ends up in the by-products no reusable catalyst
Energy costs	Low. temperature: 20–50 °C.	Medium, temperature: 60–80 °C.	High temperature: >100 °C
Catalyst cost	High	Low	Low high cost of equipment due to acid corrosion
Environmental impact	Low; wastewater treatment not needed.	High; wastewater treatment needed.	High; wastewater treatment needed.

Table 6
Review of biodiesel production from WCO using lipase from several sources.

Lipase origin	Catalyst load (wt%)	Alcohol to oil ratio	Reaction Time (h)	Reaction Temp. (°C)	Yield (%)	Ref.
Candida Antarctica	25	Methanol (25:1)	4	50	89.1	[57]
Candida Antarctica	Not specified	Propanol (3:1)	0.833	40–45	95	[56]
Thermomyces lanuginose	Not specified	Methanol (6:1)	5	65	55.5	[8]
Penicillium expansum	Not specified	Methanol (1:1)	7	35	92.8	[60]
Rhizopus oryzae	30	Methanol (4:1)	30	40	90	[61]
Bacillus subtilis	3	Methanol (1:1)	72	40	90	[62]
C. rugosa/P. fluorescens (*Mixed*)	10	Ethanol (3:1)	8	45	>67	[58]

and elimination of soap formation [75]. However, supercritical transesterification requires high reaction temperature and pressure [76,77], a large excess of alcohol, high energy consumption, and high capital cost [76]. Table 7 compares conventional and supercritical transesterification [9]. Lee et al. [78] carried out supercritical transesterification of waste canola oil and achieved a yield of approximately 100% in 45 min at 270 °C and 100 bar, with a methanol-to-oil ratio as low as 2:1. In addition, Tan et al. [79] applied methyl acetate in a 30:1 ratio at 400 °C and 220 bar to carry out a supercritical transesterification of waste oil, where the process achieved a yield of 99% within 1 h. Tan et al. [2] achieved a biodiesel yield of 80% through the supercritical transesterification of waste palm oil at 300–380 °C and 150–250 bar.

6. Alcohol type

As indicated in the previous section, alcohol is one of the main reactants in transesterification reactions. Primary and secondary monohydric aliphatic alcohols (with 1–8 carbon atoms) are mainly used in this reaction. However, methyl alcohol (methanol) and ethyl alcohol (ethanol) are also widely used for this purpose [27]. Previous reports have proposed the use of methanol for biodiesel production because of its wide availability, low cost [11], and high reactivity compared with ethanol, which minimises the reaction time [80]. However, methanol is a petroleum-based alcohol. Thus, ethanol has the advantages of being derived from renewable agricultural sources [81]. Ethanol is also more soluble in oil than methanol, which enhances mass transfer during the transesterification reaction. Moreover, biodiesel produced using ethanol (fatty acid ethyl ester, FAEE) has lower pour and cloud points than that produced using methanol (fatty acid methyl ester, FAME), which increases the storage ability of biodiesel [11]. Table 8 compares the properties of fatty acid methyl ester and fatty acid ethyl ester (Lapuerta et al.) [82].

Recently, a mixture of methanol and ethanol was used to produce biodiesel using a homogeneous base catalyst [83] and heterogeneous acid catalysts [11] and showed good results. Table 9 shows the properties of biodiesel produced using this new technology (Lam and Lee) [11].

Table 8
Comparison of properties between FAME and FAEE.

Fuel Property	Units	Ref	FAME	FAEE
Density at 15 °C	kg/m^3	834	887	878
Kinematic viscosity at 40 °C	cSt	2.72	5.16	4.92
Gross heating value	MJ/kg	45.54	39.26	39.48
Lower heating value	MJ/kg	42.49	36.59	36.81
Acid Number	mgKOH/g	0.10	0.55	0.27
% C	wt.	86.13	76.95	77.38
% H	wt.	13.87	12.14	12.19
% O	wt.	0	10.91	10.43
Sulfur content	Ppm/wt.	34	0	0
Water content	Ppm/wt.	57	466	420
Molecular weight		211.7	293.2	306.7
Iodine number		–	97.46	105.60

Table 9
Fuel properties of biodiesel derived from a mixed methanol–ethanol method.

Fuel property	Unit	Value
Density at 15 °C	(kg/m^3)	897.5
Kinematic viscosity at 40 °C	(mm^2/s)	3.55
Flash point	°C	210
Sulfur	mg/kg	0.1
Iodine value	–	56.9
Methanol content	% mass	0.1

7. Reactor type

Transesterification can be carried out discontinuously (batch) or continuously [84]. Batch transesterification usually needs a larger reactor (container) and requires longer reaction and separation time relative to continuous transesterification because all of the reaction stages are performed in the same reactor [45]. Several researchers have reported on the use of various types of reactors for the production of biodiesel from edible and non-edible oils with varying degrees of success. Conventional batch reactors have widely been used but require long times to fulfil the production capacity, which is their main drawback. Many alternatives have been studied to overcome this challenge.

An ultrasonic reactor reduces the transesterification time by a factor of 15–40 compared with conventional batch reactors (99% yield for 5 min or less agitation). It also reduces the excess alcohol required for the process and the amount of catalyst used because of its high chemical activity [85]. Membrane reactors (MRs) have been proven to minimise the wastewater produced during the process at an industrial scale, which makes it more environmentally friendly (membrane flux of 30–40 L/m^2/h, residence time of 15 min). Moreover, MRs enhance the colour and quality of methyl ester and glycerin (below the levels specified by the ASTM D6751/EN 14214 standards) [86]. On the other hand, a slit-channel reactor (1 mm channel, agitation at 200 rpm) has been used with solid catalysts (homogeneous $NaOCH_3$ annealed at 300 °C for 3 h) to produce biodiesel and has proven superior to many other reactors in terms of fabrication cost and conversion efficiency [87]. Moreover, a continuous pulsed loop reactor successfully minimises residence time and provides a continuous biodiesel production flow, thereby intensifying the process and reducing production costs (molar ratio of 6:1, oscillation frequency of 6 Hz, temperature of 60 °C, feedstock FFA contents of 0.5% (*w*/*w*) and reaction time of 10 min) [88]. A magnetically stabilised fluidised bed reactor (MSFBR) has several advantages over other continuous reactors in terms of eliminating solid mixing, low pressure drop through the bed, and ease of solid transportation (molar ratio of 8:1, 40 cm^3/min flow rate, 225 Oe magnetic field intensity, 100 min reaction time and temperature of 65 °C) [89]. Other continuous reactors, such as rotating packed bed, supercritical methanol, or gas–liquid reactors, are more effective in biodiesel production [45].

8. Downstream processing of biodiesel

The output products of the transesterification reaction are crude ester and glycerol [27]. Crude ester may consist of excess methanol, unreacted oil, catalyst residue, soap, and glycerol [28]. The purification of the final product of transesterification is one of the most important steps in the overall process [30]. The most commonly used methods in separating glycerol from crude ester are gravitational settling, centrifugation [84], and decantation funnelling [7,27]. Crude ester can then be purified by washing it with hot distilled water [84,11,27,28,90]. Washing is often carried out three times at 50 °C in separatory funnels until the washings are neutral [28]. Finally, the washed ester can be dried with magnesium sulphate [27] or molecular sieves [7] and then filtered under vacuum [7,27]. Washing crude ester with distilled water is an effective way of removing soap and other contaminants because of its solubility in water. However, this method has some disadvantages, such as product loss because of water retention

Table 10
Characterisation of three biodiesel samples purified using different techniques.

Property	Units	Purification by silica gel			Purification by 5% H_3PO_4			Purification by hot distilled water		
		MS 1	MS 2	MS 3	MS 1	MS 2	MS 3	MS 1	MS 2	MS 3
Density at 15 °C	g/cm^3	0.880	0.892	0.887	0.880	0.893	0.886	0.880	0.892	0.887
Kinematic viscosity	m^2/s	3.98	4.20	4.88	3.70	4.51	4.88	4.02	4.59	5.01
Acid value	mg KOH/g oil	0.39	0.10	0.10	0.34	0.20	0.23	0.43	0.23	0.80
Iodine number	g J$_2$/100 g	71	117	62	70	119	62	71	118	63
Water content	%	0.04	0.04	0.05	0.13	0.11	0.10	0.12	0.10	0.11
Saponification value	mg KOH/g oil	206	209	210	205	204	212	204	208	206
Cetane index	CI	56.8	47.0	58.3	57.2	46.3	58.1	57.1	46.0	58.6

during the process [84]. Thus, other purification techniques have been developed, such as dry washing with silica gel to remove traces of water [91] and wet washing using 5% phosphoric acid [90]. Table 10 shows the properties of several samples of biodiesel produced from WCO and purified with silica gel, phosphoric acid, and hot distilled water, respectively [91]. Nevertheless, there have been several attempts to recover unreacted alcohol from the output mixture of the transesterification process through stripping or vacuum distillation [27] or to remove it by flash evaporation [84] or heating the mixture to 120 °C [11]. On the other hand, the catalyst can be recovered through the ashing process at 460 °C for 5 h (Wang et al.) [33].

9. Analysis of biodiesel produced from WCO

Biodiesel analysis is performed after purification. Several analytical methods have been practiced in recent years, such as gas chromatography (GC), high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), and proton nuclear magnetic resonance (^{1}H NMR). GC is most widely used for this purpose. In this method, either helium [2,30,92,93] or nitrogen [28,33] is used as the carrier gas. Methyl heptadecanoate is also used as an internal standard (reference) [93]. There are several types of GC columns, such as the capillary column (SPB^{TM}) [33], the bench-scale batch column [30], the NukolTM fused silica capillary column [93], the Omegawax 320 capillary column [51], and the HP Innowax capillary column [28]. Tan et al. [2] introduced 1 mL of biodiesel sample into the column, with the injector and the detector kept at 220 and 250 °C, respectively. The peaks detected in the sample were compared with pure standards to determine the weight of the biodiesel produced. The yield of the reaction was then calculated based on the following equation:

$$\text{Yield,\%} = \frac{\text{Total weight of methyl ester}}{\text{Total weight of oil in the sample}} \times 100\% \quad (1)$$

Wang et al. [33] stated that biodiesel purity can be calculated based on the following equation:

$$\text{Purity,(\%)} = \frac{\text{Area of FAME/Area of reference} \times \text{Weight of reference}}{\text{Weight of crude biodiesel}} \times 100\% \quad (2)$$

On the other hand, Issariyakul et al. [83] reported on the usage of HPLC equipped with Phenogel column and tetrahydrofuran (THF) as the mobile phase. Lertsathapornsuk et al. [94] used the same method equipped with Silica 60 column and a hexane: diethyl ether: acetic acid mobile phase. Nevertheless, TLC plays a complementary role to GC. It is usually performed on glass plates coated with silica gel using visualisation solvents, such as hexane, phosphomolybdic acid [26], petroleum ether, and acetic acid [95].

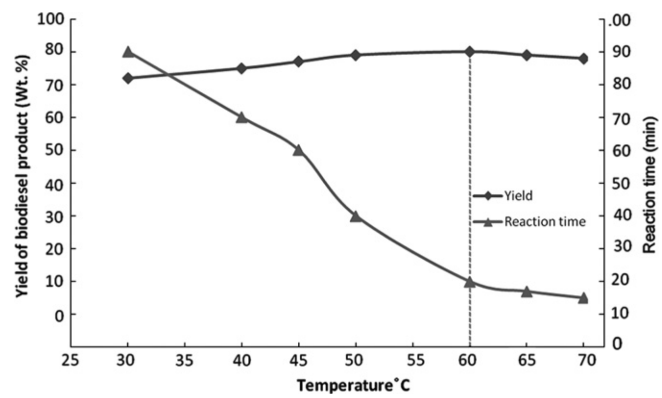


Fig. 2. Effect of temperature on the transesterification of WCO.

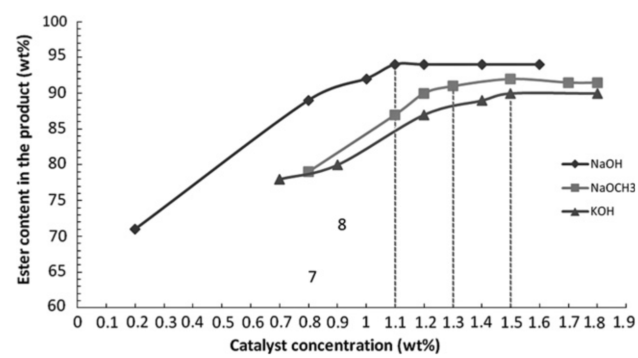


Fig. 3. Effect of different catalyst loads on the transesterification of WCO.

^{1}H NMR is an accurate, fast, and easy method relative to GC and HPLC, which do not require sample preparation [41].

10. Parametric study

The transesterification reaction depends on several parameters, such as reaction temperature, reaction time, catalyst loading, and alcohol-to-oil ratio [7,13,27–29,96]. In the following sub-sections, the effects of several parameters on biodiesel yield are studied with the aid of graphs based on previous research.

10.1. Effect of temperature

Although transesterification reaction can be performed at room temperature, the process is strongly influenced by the reaction temperature [27]. According to Cvengros and Cvengrosova [18], the ideal reaction temperature is often near the boiling point of alcohol. However, the reaction can be carried out at

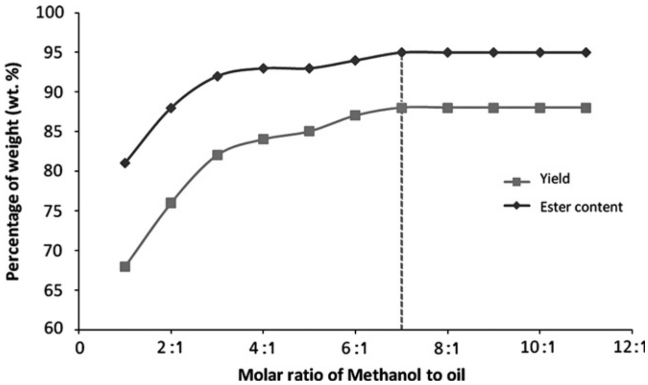


Fig. 4. Effect of alcohol-to-oil ratio on the transesterification of WCO.

Table 11
Average prices of selected oils used in biodiesel production in 2007.

Oil	Price (US$/ton)
Crude palm oil	703
Rapeseed oil	824
Soybean oil	771
WCO	224
Yellow grease	412

Table 12
Estimated required selling price of biodiesel by supercritical transesterification in US.

Plant capacity (tones/year)	125,000	80,000	8,000
Fixed capital	10,395,058	7,953,072	1,997,721
Working capital	1,661,348	1,513,014	313,729
Start up cost	4,984,045	4,539,042	941,187
Total capital cost	17,040,452	14,005,128	3,252,638
Annual variable cost			
Raw material			
WCO	26,068,993	16,784,050	1,709,129
Methanol	4,218,750	2,736,000	278,400
Total raw materials cost	30,287,743	19,520,050	1,987,529
Start up			
Methanol	14,400	9,050	924
Propane	4,409	2,672	269
Total start up cost	18,809	11,722	1,193
Utilities			
Electricity	713,592	456,699	45,670
Cooling water	102,708	67,103	8,217
Biodiesel for the reboiler	978,359	872,157	198,371
Total utilities cost	1,794,660	1,395,958	252,257
By-product credit			
Glycerol	15,973,500	6,234,000	1,017,600
Fixed cost			
Operating labor	1,020,000	1,020,000	1,020,000
Maintenance	485,103	371,143	371,143
Plant overhead	913,021	890,229	890,229
Taxes and insurance	207,901	159,061	39,954
Total fixed cost	2,626,024	2,440,433	2,321,326
Total operating cost	18,789,736	17,134,165	3,538,992
Capital charges[a]	5,314,381	4,353,483	1,207,569
S, G & A	1,205,206	1,074,382	237,328
Required Selling Price	25,309,323	22,562,030	4,983,890
RSP (US$/tones)	202	282	623
RSP (US$/kg)	0.20	0.28	0.26
RSP (US$/l)	0.17	0.24	0.52

[a] 20% return of investment (ROI) used.

different temperatures, depending on the physical and chemical properties of the oil used [13]. Several studies reported that 50–70 °C would be the best temperature range to obtain the highest biodiesel yield [28]. However, Chen et al. [7] reported that transesterification process, with a lipase catalyst, should not be carried out above 50 °C because the stability and the usage life of lipase may be affected. Fig. 2 shows the effect of temperature on the transesterification of WCO [27].

10.2. Catalyst loading

The catalyst content is also dependent on the type of oil used in the transesterification process and the type of catalyst. Thus, the optimum load of alkali catalysts, such as NaOH, for WCO transesterification is approximately 1.0 wt% [13,28]. In contrast, for acid catalysts, the load can be up to 4%. According to Wang et al. [33], when the amount of sulphur acid exceeds 4%, no sufficient increment of conversion occurs. The effect of three different basic catalysts on biodiesel yield is shown in Fig. 3 [27]. Nevertheless, Chen et al. [7] stated that enzyme activity increases with increasing content. Thus, a 25% enzyme load is the most feasible for obtaining the highest possible biodiesel yield.

10.3. Effect of alcohol-to-oil ratio

Transesterification reactions are reversible. Thus, excess alcohol is needed to shift the reaction toward the forward direction [27]. Therefore, the alcohol-to-oil ratio is one of the most sensitive factors that affect the final biodiesel yield [96]. Meng et al. [28] revealed that, in the presence of a sodium hydroxide catalyst, the optimum methanol-to-WCO ratio is approximately 5:1. In contrast, Banerjee and Chakraborty [27] reported that a 100% excess of alcohol maximises the reaction rate (Fig. 4).

11. Cost estimation and feasibility studies

In the past few years, several studies have been carried out to produce biodiesel at a minimum total production cost to compete with conventional diesel [2]. These studies found that the cost of feedstock (raw oil) is more than 70% of the total cost [13,44]. Thus, research has been intensified to find a substitute to expensive virgin vegetable oils. WCO is one of the most suitable alternatives (Table 11) [97].

Van Kasteren and Nisworo [9] carried out feasibility studies on a biodiesel production plant using WCO as feedstock and implementing the supercritical transesterification process (in the absence of a catalyst). They found that the major contributors to biodiesel price are the price of raw oil (71–80%) and capital cost (15–16%). Additionally, the production of glycerol as a byproduct may reduce the price of biodiesel by 22–36% of the total cost because it can be utilised in several applications, such as pharmaceuticals, food industries, cosmetics, lubricants, and intermediates [98]. In addition, Zhang et al. [6] stated that the main economic criteria for biodiesel production based on previous studies were capital cost, manufacturing cost, and biodiesel break-even cost. Table 12 shows the estimated required selling price of biodiesel from WCO in the United States [9].

12. Conclusion

Regarding the production of biodiesel from waste cooking oil (WCO), the following important key points have been highlighted:

1. Biodiesel has been proven the best substitute to fossil fuel. It is superior to petroleum-based fuels because it is renewable, biodegradable, and non-toxic.
2. Several edible oils have been use as WCO feedstock in biodiesel production, such as sunflower oil, palm oil, soybean oil and olive oil.
3. Transesterification is more common in the production of biodiesel than other conversion processes, such as micro-emulsification and pyrolysis.
4. WCO is expected to be more important in the future production of biodiesel than other edible and non-edible oils because of its low cost and wide availability. However, WCO requires several pre-treatment steps to eliminate solid impurities and reduce FFA and water contents. The pre-treatment process may include a washing step, centrifugation, flash evaporation, and acid esterification.
5. Several types of catalysts have been used widely for esterification reaction, such as homogenous catalysts (acidic and basic), heterogeneous catalysts (acidic and basic), and enzymes. Base homogenous catalysts face a large challenge in terms of the FFA and water contents in the oil. Therefore, a two-step process may overcome this challenge. Nevertheless, lipase enzyme is able to overcome this challenge and provide purer biodiesel and an easier system to separate the glycerol. However, this practice is not used at an industrial scale because of its high cost and time consumption.
6. Methanol is used in the transesterification process because of its wide availability, high activity, and low cost. However, ethanol is more soluble in oil, which enhances mass transfer within the system. Thus, a methanol–ethanol mixture was proposed to combine the advantages of both alcohols.

References

[1] Wan Omar WNN, Saidina Amin NA. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass and Bioenergy 2011;35:1329–38.
[2] Tan KT, Lee KT, Mohamed AR. Potential of waste palm cooking oil for catalyst-free biodiesel production. Energy 2011;36:2085–8.
[3] Demirbas A. Progress and recent trends in biodiesel fuels. Energy Conversion and Management 2009;50:14–34.
[4] Dizge N, Aydiner C, Imer DY, Bayramoglu M, Tanriseven A, Keskinler B. Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. Bioresource Technology 2009;100:1983–91.
[5] Campanelli P, Banchero M, Manna L. Synthesis of biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification. Fuel 2010;89:3675–82.
[6] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresource Technology 2003;90:229–40.
[7] Chen Y, Xiao B, Chang J, Fu Y, Lv P, Wang X. Synthesis of biodiesel from waste cooking oil using immobilized lipase in fixed bed reactor. Energy Conversion and Management 2009;50:668–73.
[8] N Avlijaš and F Nappi, Collection of used vegetable oil: experiences around Europe. In: 1st biosire international workshop, Heraklion, Crete. September 14th 2009.
[9] Van Kasteren JMN, Nisworo AP. A process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification. Resources, Conservation and Recycling 2007;50:442–58.
[10] Yusuf NNAN, Kamarudin SK, Yaakob Z. Overview on the current trends in biodiesel production. Energy Conversion and Management 2011;52: 2741–51.
[11] Lam MK, Lee KT. Mixed methanol–ethanol technology to produce greener biodiesel from waste cooking oil: a breakthrough for $SO_{42-}/SnO_2–SiO_2$ catalyst. Fuel Processing Technology 2011;92:1639–45.
[12] Knothe G, Sharp C, Ryan T. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. Energy Fuel 2006;20:403–8.
[13] Phan AN, Phan TM. Biodiesel production from waste cooking oils. Fuel 2008;87:3490–6.
[14] Demirbas A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. Energy Conversion and Management 2009;50:923–7.
[15] Knothe G, Steidley KR. A comparison of used cooking oils: a very heterogeneous feedstock for biodiesel. Bioresource Technology 2009;100: 5796–801.
[16] Demirbas A. Biodiesel: a realistic fuel alternative for diesel engines. London: Springer; 2008.
[17] Demirbas A. New liquid biofuels from vegetable oils via catalytic pyrolysis. Energy Education Science and Technology 2008;21:1–59.
[18] Cvengros J, Cvengrosova Z. Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids. Biomass Bioenergy 2004;27:173–81.
[19] Wen Z, Yu X, Tu S-T, Yan J, Dahlquist E. Biodiesel production from waste cooking oil catalyzed by TiO_2–MgO mixed oxides. Bioresource Technology 2010;101:9570–6.
[20] Gui MM, Lee KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Energy 2008;33:1646–53.
[21] Kulkarni MG, Dalai AK. Waste cooking oils an economical source for biodiesel. Industrial and Engineering Chemistry Research 2006;45:2901–13.
[22] H Imahara, E Minami, M Hattori, H Murakami, N Matsui, S Saka, Current situations and prospects of oil/fat resources for biodiesel production. In: Joint international conference on sustainable energy and environment (SEE 2006), Bangkok, Thailand. November 2006.
[23] Tsai WT, Lin CC, Yeh CW. An analysis of biodiesel fuel from waste edible oil in Taiwan. Renewable & Sustainable Energy Reviews 2007;11:838–57.
[24] F Berruti and C Briens. Industrial and commercial fats, oils and greases. Final Report. Green fuels and chemicals—GPE 4484/CBE 9334. Faculty of engineering. The University of Western Ontario (2011).
[25] Diya'uddeen BH, Aziz ARA, Daud WMAW, Chakrabarti MH. Performance evaluation of biodiesel from used domestic waste oils: a review. Process Safety and Environmental Protection 2012;90:164–79.
[26] Leung D, Guo Y. Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Process Technology 2006:883–90.
[27] Banerjee A, Chakraborty R. Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—a review. Resources, Conservation and Recycling 2009;53:490–7.
[28] Meng X, Chen G, Wang Y. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. Fuel Processing Technology 2008;89: 851–7.
[29] Özbay N, Oktar N, Tapan N. Esterification of free fatty acids in waste cooking oils (WCO): role of ion-exchange resins. Fuel 2008;87:1789–98.
[30] Felizardo P, Neiva CM, Raposo I, Mendes J, Berkemeier R, Bordado J. Production of biodiesel from waste frying oils. Waste Management 2006;26: 487–94.
[31] Freedman B, Pryde E, Mounts T. Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of the American Oil Chemists Society 1984:1638–43.
[32] Ma F, Hanna M. Biodiesel production: a review. Bioresource Technology 1999;70:1–15.
[33] Wang Y, Ou S, Liu P, Xue F, Tang S. Comparison of two different processes to synthesize biodiesel by waste cooking oil. Journal of Molecular Catalysis A: Chemical 2006;252:107–12.
[34] Mittelbach M, Enzelsberger H. Transesterification of heated rapeseed oil for extending diesel fuel. Journal of the American Oil Chemists Society 1999;76:545–50.
[35] Sharma YC, Singh B. Development of biodiesel from karanja, a tree found in rural India. Fuel 2008;67:1740–2.
[36] Patil P, Deng S, Isaac Rhodes J, Lammers PJ. Conversion of waste cooking oil to biodiesel using ferric sulfate and supercritical methanol processes. Fuel 2010;89:360–4.
[37] Shimada Y, Watanabe Y, Sugihara A, Tominaga Y. Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing. Journal of Molecular Catalysis B: Enzymatic 2002;17:133–42.
[38] Georgogianni KG, Katsoulidis AK, Pomonis PJ, Manos G, Kontominas MG. Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. Fuel Processing Technology 2009;90:1016–22.
[39] Vicente G, Martı´nez M, Aracil J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresource Technology 2004;92: 297–305.
[40] Soriano Jr NU, Venditti R, Argyropoulos DS. Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. Fuel 2009;88:560–5.
[41] Guzatto R, de Martini TL, Samios D. The use of a modified TDSP for biodiesel production from soybean, linseed and waste cooking oil. Fuel Processing Technology 2011;92:2083–8.
[42] Wang Y, Ou PLS, Zhang Z. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. Energy Conversion and Management 2007;48: 184–8.
[43] Çaylı G, Küsefoğlu GS. Increased yields in biodiesel production from used cooking oils by a two step process: comparison with one step process by using TGA. Fuel Processing Technology 2008;89:118–22.
[44] Bautista LF, Vicente G, Rodríguez R, Pacheco M. Optimisation of FAME production from waste cooking oil for biodiesel use. Biomass and Bioenergy 2009;33:862–72.
[45] Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: a practical and economical approach to produce high quality biodiesel fuel. Bioresource Technology 2010;101:5394–401.

[46] Charoenchaitrakool M, Thienmethangkoon J. Statistical optimization for biodiesel production from waste frying oil through two-step catalyzed process. Fuel Processing Technology 2011;92:112–8.
[47] Yan J, Yan Y, Liu S, Hu J, Wang G. Preparation of cross-linked lipase-coated micro-crystals for biodiesel production from waste cooking oil. Bioresource Technology 2011;102:4755–8.
[48] Kiss FE, Jovanović M, Bošković GC. Economic and ecological aspects of biodiesel production over homogeneous and heterogeneous catalysts. Fuel Processing Technology 2010;91:1316–20.
[49] Agarwal M, Chauhan G, Chaurasia SP, Singh K. Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. Journal of the Taiwan Institute of Chemical Engineers 2012;43:89–94.
[50] Sakai T, Kawashima A, Koshikawa T. Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. Bioresource Technology 2009;100:3268–76.
[51] Chakraborty R, Das SK. Optimization of biodiesel synthesis from waste frying soybean oil using fish scale-supported Ni catalyst. Industrial and Engineering Chemistry Research 2012;51:404–8414.
[52] Akbar E, Narayanan B, Yaakob Z, Kamarudin SK, Salimon J. Preparation of Na doped SiO_2 solid catalysts by the sol–gel method for the production of biodiesel from jatropha oil. Green Chemistry 2009;11:1862–6.
[53] Yusuf NNAN, Kamarudin SK, Yaakob Z. Overview on the production of biodiesel from jatropha curcas L. by using Heterogenous catalysts, biofuel. Bioproduct and Bio-refinery 2012.
[54] Yaakob Z, Sukarman IS, Narayanan B, Abdullah SRS, Ismail M. Utilization of palm empty fruit bunch for the production of biodiesel from jatropha curcas oil. Bioresource Technology 2012;104:695–700.
[55] Chakraborty R, Bepari S, Banerjee A. Application of calcined waste fish (Labeo rohita) scale as low-cost heterogeneous catalyst for biodiesel synthesis. Ioresource Technology 2011;102:3610–8.
[56] Chakraborty R, Bepari S, Banerjee A. Transesterification of soybean oil catalyzed by fly ash and egg shell derived solid catalysts. Chemical Engineering Journal 2010;165:798–805.
[57] Wan Omar WNN, Saidina Amin NA. Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. Fuel Processing Technology 2011;92:2397–405.
[58] Al-Zuhair S, Dowaidar A, Kamal H. Dynamic modeling of biodiesel production from simulated waste cooking oil using immobilized lipase. Biochemical Engineering Journal 2009;44:256–62.
[59] Hama S, Tamalampudi S, Yoshida A, Tamadani N, Kuratani N, Noda H, et al. A. Process engineering and optimization of glycerol separation in a packed-bed reactor for enzymatic biodiesel production. Bioresource Technology 2011;102:10419–24.
[60] Ranganathan SV, Narasimhan SL, Muthukumar K. An overview of enzymatic production of biodiesel. Bioresource Technology 2008;99:3975–81.
[61] Talukder MMR, Das P, Fang TS, Wu JC. Enhanced enzymatic transesterification of palm oil to biodiesel. Biochemical Engineering Journal 2011;55: 119–22.
[62] Gog A, Roman M, Toşa M, Paizs C, Irimie FD. Biodiesel production using enzymatic transesterification—current state and perspectives. Renewable Energy 2012;39:10–6.
[63] Antczak MS, Kubiak A, Antczak T, Bielecki S. Enzymatic biodiesel synthesis—key factors affecting efficiency of the process. Renewable Energy 2009;34:1185–94.
[64] Wang J-X, Huang Q-D, Huang F-H, Wang J-W, Huang Q-J. Lipase-catalyzed production of biodiesel from high acid value waste oil using ultrasonic assistant. Chinese Journal of Biotechnology 2007;23:1121–8.
[65] Maceiras R, Vega M, Costa C, Ramos P, Márquez MC. Effect of methanol content on enzymatic production of biodiesel from waste frying oil. Fuel 2009;88:2130–4.
[66] Tongboriboon K, Cheirsilp B, H-Kittikun A. Mixed lipases for efficient enzymatic synthesis of biodiesel from used palm oil and ethanol in a solvent-free system. Journal of Molecular Catalysis B: Enzymatic 2010;67:52–9.
[67] Al-Zuhair S, Ling FW, Jun LS. Proposed kinetic mechanism of the production of biodiesel from palm oil using lipase. Process Biochemistry 2007;42: 951–60.
[68] Li N-W, Zong M-H, Wu H. Highly efficient transformation of waste oil to biodiesel by immobilized lipase from *Penicillium expansum*. Process Biochemistry 2009;44:685–8.
[69] Chen G, Ying M, Li W. Enzymatic conversion of waste cooking oils into alternative fuel—biodiesel. Applied Biochemistry and Biotechnology 2006;132: 911–21.
[70] Ying M, Chen G. Study on the production of biodiesel by magnetic cell biocatalyst based on lipase-producing *Bacillus subtilis*. Applied Biochemistry and Biotechnology 2007;137–140:793–803.
[71] Hama S, Tamalampudi S, Yoshida A, Tamadani N, Kuratani N, Noda H, et al. packed-bed reactor integrated with glycerol-separating system for solvent-free production of biodiesel fuel. Biochemical Engineering Journal 2011;55:66–71.
[72] Rodrigues AR, Paiva A, da Silva MG, Simões P, Barreiros S. Continuous enzymatic production of biodiesel from virgin and waste sunflower oil in supercritical carbon dioxide. The Journal of Supercritical Fluids 2011;56:259–64.
[73] Xin J, Imahara H, Saka S. Oxidation stability of biodiesel fuel as prepared by supercritical methanol. Fuel 2008;87:1807–13.
[74] Saka S, Isayama Y. A new process for catalyst-free production of biodiesel using supercritical methyl acetate. Fuel 2009;88:1307–13.
[75] Quesada-Medina J, Olivares-Carrillo P. Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol. The Journal of Supercritical Fluids 2011;56:56–63.
[76] Saka S, Isayama Y, Ilham Z, Jiayu X. New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol. Fuel 2010;89:1442–6.
[77] Tan KT, Lee KT, Mohamed AR. Effects of free fatty acids, water content and co-solvent on biodiesel production by supercritical methanol reaction. The Journal of Supercritical Fluids 2010;53:88–91.
[78] Lee S, Posarac D, Ellis N. An experimental investigation of biodiesel synthesis from waste canola oil using supercritical methanol. Fuel 2012;91:229–37.
[79] Tan KT, Lee KT, Mohamed AR. Prospects of non-catalytic supercritical methyl acetate process in biodiesel production. Fuel Processing Technology 2011;92:1905–9.
[80] Meneghetti S, Meneghetti M, Wolf C, Silva E, Lima G, de Lira Silva L, et al. Biodiesel from castor oil: a comparison of ethanolysis versus methanolysis. Energy & Fuels 2006;20:2262–5.
[81] Encinar JM, Gonzaìlez JF, Rodrıìguez-Reinares A. Ethanolysis of used frying oil. Biodiesel preparation and characterization. Fuel Processing Technology 2007:513–22.
[82] Lapuerta M, Herreros JM, Lyons LL, García-Contreras R, Briceño Y. Effect of the alcohol type used in the production of waste cooking oil biodiesel on diesel performance and emissions. Fuel 2008;87:3161–9.
[83] Issariyakul T, Kulkarni MG, Dalai AK, Bakhshi NN. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. Fuel Processing Technology 2007:429–36.
[84] Berrios M, Martín MA, Chica AF, Martín A. Purification of biodiesel from used cooking oils. Applied Energy 2011;88:3625–31.
[85] Singh AK, Fernando SD, Hernandez R. Base-catalyzed fast transesterification of soybean oil using ultrasonication. Energy Fuels 2007;21:1161–4.
[86] Falahati H, Tremblay AY. The effect of flux and residence time in the production of biodiesel from various feedstocks using a membrane reactor. Fuel 2012;91:126–33.
[87] Kalu EE, Chen KS, Gedris T. Continuous-flow biodiesel production using slit-channel reactors. Bioresource Technology 2011;102:4456–61.
[88] Syam AM, Yunus R, Ghazi TIM, Choong TSY. Synthesis of jatropha curcas oil-based biodiesel in a pulsed loop reactor. Industrial Crops and Products 2011.
[89] Guo P, Huang F, Huang Q, Zheng C. Biodiesel production using magnetically stabilized fluidized bed reactor. Renewable Energy 2012;38:10–5.
[90] Hingu SM, Gogate PR, Rathod VK. Synthesis of biodiesel from waste cooking oil using sonochemical reactors. Ultrasonics Sonochemistry 2010;17:827–32.
[91] Zlatica JP. The production of biodiesel from waste frying oils: a comparison of different purification steps. Fuel 2008;87:3522–8.
[92] Alcantara R, Amores J, Canoira L, Fidalgo E, Franco MJ, Navarro A. Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. Biomass and Bioenergy 2000;18:515–27.
[93] Halim SFA, Kamaruddin AH, Fernando WJN. Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: optimization using response surface methodology (RSM) and mass transfer studies. Bioresource Technology 2009;100:710–6.
[94] Lertsathapornsuk V, Pairintra R, Aryusuk K, Krisnangkura K. Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. Fuel Processing Technology 2008;89:1330–6.
[95] Tomasevic AV, Siler-Marinkovic SS. Methanolysis of used frying oil. Fuel Processing Technology 2003;81:1–6.
[96] Jacobson K, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production from waste cooking oil. Applied Catalysis B: Environmental 2008;85:86–91.
[97] Demirbas A. Economic and environmental impacts of the liquid biofuels. Energy Education Science and Technology 2008:37–58.
[98] Pagliaro M, Ciriminna R, Kimura H, Rossi M, Della PC. From glycerol to value-added products. Angewandte Chemie International Edition 2007:4434–40.